Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

THE CHLORIDE PROCESSING OF LEAD CONCENTRATES

J.E. Dutrizac
Metallurgical Chemistry Section
Extractive Metallurgy Laboratory

April 1984

Project: MRP-3.4.0.2.02
Hydrometallurgical Lead Process

MAY 18 1984
MICROMEDIA

This document is an unedited interim report prepared [illegible] for discussion and [illegible] reporting purposes [illegible] represent a final [illegible] the opinion of the [illegible] for Mineral and Energy Technology (CANMET)

Ce document est un rapport provisoire non-révisé et rédigé [illegible] pour fin de [illegible] et de documentation [illegible] Il ne représente nullement [illegible] définitive de l'opinion du Centre canadien de la technologie des minéraux et de l'énergie (CANMET)

47 pp

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT MRP/MSL 84-41 (LS)

Crown Copyrights Reserved

THE CHLORIDE PROCESSING OF LEAD CONCENTRATES

by

J.E. Dutrizac*

ABSTRACT

The extensive body of recently published work on the ferric chloride and/or cupric chloride leaching of lead concentrates, as well as on the related topics of solution purification and metal recovery, has been reviewed and evaluated. A wide variety of processes have been developed that strive to utilize the rapid leaching rates, elemental sulphur formation and inherently hygienic nature of the process. Although several options have been developed, none has yet achieved industrial acceptance. Major problems have been identified with both lead metal production and the recovery of silver. Impurity control will likely also be difficult in such processes. There is a continuing need for both large-scale process development as well as fundamental studies on all aspects of this type of technology.

---

* Research Scientist, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, 555 Booth Street, Ottawa, Ontario, K1A 0G1.

TRAITEMENT AU CHLORURE DES CONCENTRES DE PLOMB

par

J.E. Dutrizac*

RESUME

On a revu et évalué les nombreuses publications parues récemment sur l'extraction au chlorure ferrique et/ou au chlorure cuivrique des concentrés de plomb et sur les procédés apparentés que sont la purification des solutions et la récupération des métaux. On a mis au point un très grand nombre de procédés qui exploitent les vitesses élevées d'extraction, la formation de soufre élémentaire et la nature hygiénique du processus. Plusieurs options ont été mises au point, mais aucune n'a encore été adoptée par l'industrie. On a cerné les principaux problèmes associés à la production de plomb métallique et à la récupération de l'argent. L'élimination des impuretés constituera vraisemblablement un problème. Il y a lieu de poursuivre le développement à grande échelle de ce procédé et de continuer les études fondamentales sur tous les aspects de ce type de technologie.

---

* Chercheur, Laboratoires des sciences minérales, CANMET, Ministère de l'Energie, des Mines et des Ressources, 555, rue Booth, Ottawa (Ontario) K1A 0G1.

INTRODUCTION

The processing of lead concentrates should be an obvious and potentially attractive application of hydrometallurgical methods. The hydrometallurgical route can likely overcome the in-plant hygiene problems associated with lead-bearing dusts and fumes produced during conventional pyrometallurgical processing (U.S. ambient air regulations for the workplace are 50 µg Pb/m^3), and by forming elemental sulphur, avoids the costly task of collecting and treating dilute SO_2 gas streams emanating from conventional sinter units. Also, the aqueous approach could greatly simplify the complex fire or electrorefining methods currently used for lead bullion. The overall simplicity of operation could result in lower capital costs for the aqueous route, especially for smaller operations. Although concentrated hydrochloric acid solutions offer some advantages, most activity has centered on the use of ferric chloride or cupric chloride media. Lead is rapidly leached in either ferric chloride or cupric chloride media with the formation of elemental sulphur. A useful $PbCl_2$ intermediary product of high purity is easily formed and lead recovery from $PbCl_2$ seems reasonably straightforward. Although trace element (e.g., Ag, As, Cu, SO_4, etc.) deportment still presents some technical difficulties for the hydrometallurgical route, the attractive features of aqueous processing have been sufficiently compelling to prompt considerable activity in this field.

Several years ago, the U.S. Bureau of Mines (1) evaluated many hydrometallurgical methods for processing lead concentrates including:

a) Direct electrolysis of the concentrate in a molten salt bath

b) Amine leaching processes

c) Caustic fusion

d) Leaching with strong oxidants such as Cl_2, H_2O_2, NaOCl, O_3 or $KMnO_4$

e) Ferric sulphate leaching followed by eventual metal electrolysis from fluosilicic acid

f) Ferric chloride leaching followed by fused salt electrolysis

The underlying objective of all the test work was to avoid SO_2 emissions via the formation of elemental sulphur. Of the methods evaluated, only the ferric ion-based technologies (and certainly $CuCl_2$ as well) appeared capable of yielding an acceptable sulphur product. Although initial work favoured the ferric sulphate approach, the ferric chloride option was finally chosen and subsequently extensively tested at the pilot-plant scale by a Bureau of Mines - Industry consortium. More recently, Correa (2) evaluated leaching for lead processing and also concluded that the chloride option was superior to nitric acid, hydrochloric acid or cyanide leaching. Bounds (3) discussed the future of lead processing and felt that projected environmental-hygiene regulations might make lead pyrometallurgy uneconomical. He too believed that chloride-based technologies were very promising for lead and discussed the strengths and weaknesses of three of the more developed processes. Tentative costs of an "idealized" $FeCl_3$ leach process were offered; operating costs were estimated at $0.187/kg and the capital cost of a 100,000 stpy plant was calculated to be $100,000,000. The projected costs, although obviously very approximate, were sufficiently encouraging to warrant further work.

Because of the advantages of the ferric chloride-cupric chloride option, extensive process development work has taken place during the past 10-15 years. In addition, a number of fundamental or related studies have also been carried out during that period. The purpose of the current literature review is to discuss and evaluate that body of recently published work with special reference to CANMET's Hydrometallurgical Lead Process Project.

PROCESS DEVELOPMENT - LOW TEMPERATURE PROCESSES

The Hecla Mining Company (4,5) developed a ferric chloride process for recovering lead and silver from galena-tetrahedrite concentrates; these are particularly difficult to process hydrometallurgically since much of the silver is associated with the refractory tetrahedrite mineralization. The process, Figure 1, involves leaching at ∿50°C for 2 h with a stoichiometric excess of concentrated ferric chloride (3-4 M $FeCl_3$) media to convert galena to largely insoluble $PbCl_2$ and elemental sulphur. Silver reports as AgCl and is also mostly insoluble.

$$PbS + 2FeCl_3 \longrightarrow PbCl_2 + 2FeCl_2 + S^o \quad (1)$$

$$Ag_2S + 2FeCl_3 \longrightarrow 2AgCl + 2FeCl_2 + S^o \quad (2)$$

By conducting the leaching at low temperatures for relatively short times, other impurity sulphides like pyrite, sphalerite or chalcopyrite are hardly attacked, and this is a processing advantage if the amount of such impurities is too low to warrent their recovery. The leach residue containing most of the lead and silver is separated from the spent solution which is then oxidized and recycled to the leaching stage. The residue is subsequently leached in hot, 250-350 g/L NaCl brine for ½-2 h to extract the chlorides of lead and silver. After separation of the residue from the brine in a hot centrifuge, the solution is cooled to ∿25°C to crystallize relatively pure $PbCl_2$ which is dried and subjected to fused salt electrolysis in a $PbCl_2$-NaCl medium. The bulk of the silver remains in the brine solution from which it can be recuperated by cementation on copper. Minor impurity buildup was controlled by treating a bleed stream with iron powder to recover lead and copper.

$$Cu^{2+} + Fe^o \longrightarrow Cu^o + Fe^{2+} \quad (3)$$

$$Pb^{2+} + Fe^o \longrightarrow Pb^o + Fe^{2+} \quad (4)$$

The solution was then treated with Na_2S and/or lime to precipitate zinc and iron.

$$Zn^{2+} + S^{2-} \longrightarrow ZnS \qquad (5)$$

$$Fe^{2+} + CaO + H_2O \longrightarrow Fe(OH)_2 + Ca^{2+} \qquad (6)$$

The cementation of both Pb and Ag from chloride media has been reported by Hamdorf (6) and it seems that the reaction is rapid and is first-order chemically controlled for Pb; Ag cementation is diffusional controlled.

The disadvantage of any low temperature chloride leaching process is that many mineral forms of silver are not readily converted to AgCl and, hence, are not extensively recovered. This is especially true of the common mineral tetrahedrite, $(Cu,Ag)_{12}Sb_4S_{13}$, which was present in all the concentrates evaluated by Hecla Mining. Two methods were considered by Hecla to enhance the extent of silver recovery. In the first, the unleached tetrahedrite remaining in the leach residue was treated for 2-20 h with 50-300 g/L S^{2-} as Na_2S at $\sim 100^{\circ}C$ to convert the tetrahedrite to leachable Ag_2S-$Cu(Ag)_2S$ and soluble sodium antimonate. After liquid-solid separation, the silver-bearing residue was again leached with $FeCl_3$ to dissolve the silver. With this recovery option, the total extraction of Pb was 99.9% and of Ag was 96.9%. The second, and preferred, option for enhancing silver recoveries from galena-tetrahedrite concentrates involves a preliminary decomposition roast at 550-900°C for ~1.5 h in a neutral or reducing atmosphere to decompose the tetrahedrite prior to $FeCl_3$ leaching. The flowsheet for the preferred low-temperature leaching option is given in Figure 1. The preliminary decomposition roast was found to enhance both lead and silver recoveries while simultaneously reducing the extent of zinc dissolution. The mechanism by which the reducing roast works is not fully understood but

clearly involves a decomposition of tetrahedrite into simpler, and more readily leachable phases.

$$(Cu,Ag)_{12}Sb_4S_{13} \xrightarrow{>550^{\circ}C} 6(Cu,Ag)_2S + 2Sb_2S_3 + S^{\circ} \qquad (7)$$

Cominco Limited (7,8) has also developed a low temperature ferric chloride leaching process for both high-grade and low-grade lead concentrates. Their leaching step was done for 4 h at 40°C using a 120 g/L Fe^{3+} medium containing minor free acid (1.5 g/L HCl); the molar ratio of Fe^{3+}/Pb was 2.4. During the leaching stage, the lead was converted to largely insoluble $PbCl_2$ while most of the other base metal sulphides were unaffected. A large portion of the Ag and Bi dissolved and this is indicative of the absence of large amounts of Ag-bearing tetrahedrite in their feeds. The resulting slurry was readily filtered to produce a ferrous chloride spent liquor and a $PbCl_2$-bearing residue which was subsequently brine leached at 90-95°C in 300 g/L NaCl media to solubilize the lead.

$$PbCl_2 + 2NaCl \longrightarrow PbCl_4^{2-} + 2Na^{+} \qquad (8)$$

After hot filtration, the solution was cooled to 25-30°C to precipitate relatively pure $PbCl_2$ crystals. The brine leach step was found to be energy intensive, and efforts were made to optimize the amount of lead extracted in each stage. The $PbCl_2$ crystals were electrolyzed in a molten 92% $PbCl_2$ - 8% NaCl bath at ~500°C to yield lead at a high current efficiency (>98%) and chlorine gas which was used to regenerate the lixiviant at 40-45°C.

Even at the 40°C leaching temperature, the leach liquor dissolves many impurities, and of course, requires purification. Cominco devised a sophisticated purification procedure to purify a small (~10%) bleed stream of the spent leach liquor, and their flowsheet is shown in Figure 2. After initial evaporation to maintain the water balance, the solution is treated with excess concentrate

at 50°C to reduce residual Fe^{3+} to Fe^{2+}. The excess concentrate is filtered off and is sent to the main leach circuit. Minor elements such as Cu, Ag, Bi, Sb, As and Pb are eliminated as sulphides by the addition of H_2S gas at ambient temperature and pressure; this precipitate is the major silver product of the process alth gh the presence of the impurity elements could create processing difficulties. Zinc is controlled by H_2S addition at a pH maintained at 1.5; the product is a suitable feed for a zinc plant.

$$ZnCl_2 + CaO + H_2S \longrightarrow ZnS + CaCl_2 + H_2O \qquad (9)$$

Calcium is regulated by the addition of excess H_2SO_4 to precipitate some hydrate or hydrates of calcium sulphate.

$$CaCl_2 + H_2SO_4 + xH_2O \longrightarrow CaSO_4.xH_2O + 2HCl \qquad (10)$$

The excess acid must then be eliminated, and this is accomplished by the addition of concentrate at 90°C to form H_2S for use earlier in the purification circuit.

$$2HCl + PbS \longrightarrow PbCl_2 + H_2S \qquad (11)$$

Any leaching process will dissolve some excess iron, and in the Cominco process this is regulated by hydrolysis of a small bleed stream at 170°C and 100 psi O_2 pressure.

$$3FeCl_2 + 3/4\ O_2 \longrightarrow 2FeCl_3 + \tfrac{1}{2}Fe_2O_3 \qquad (12)$$

Finally, the solution is reoxidized with Cl_2 gas from the electrolysis circuit and is recycled to the leaching stage. Although the Cominco flowsheet adds excess H_2SO_4 to control calcium, experience at CANMET suggests that it may be desirable to operate the circuit with an excess of $CaCl_2$ and to use the calcium to control sulphate rather than vice versa. Calcium seems to cause no problems in the circuit whereas sulphate eventually concentrates in the fused salt bath.

The Reynolds process (9) is likewise a low temperature approach, but employs cupric chloride leaching in place of $FeCl_3$ attack. The lead concentrate is leached for 1-4 h at 30-60°C with 8-25 g/L $CuCl_2$ to form $PbCl_2$ and elemental sulphur.

$$2CuCl_2 + PbS \longrightarrow 2CuCl + PbCl_2 + S^o \qquad (13)$$

The leach is run under slightly oxidizing conditions (350-400 mV SCE) to prevent H_2S evolution; air sparging during the leaching stage is recommended. The leaching solution also contains 100-250 g/L NaCl which helps to stabilize the cuprous ion reaction product. After filtration, the lead chloride-bearing residue is leached in concentrated brine in an autoclave at 100-170°C; the brine contains 210-250 g/L NaCl. Although the use of an autoclave imposes additional costs on the process, it is claimed to give a high lead solubility in a short period; retention times of 0.5-5 min are adequate to yield 130 g Pb/L, a very high solubility of $PbCl_2$ indeed. After liquid-solid separation at the elevated temperature used for the $PbCl_2$ extraction, $PbCl_2$ crystals are formed by flash cooling-evaporation to <40°C. In the Reynolds process, metallic lead is produced by hydrogen reduction of the dried $PbCl_2$ crystals at 600-900°C with excess H_2.

$$PbCl_2 + H_2 \longrightarrow HCl + Pb^o \qquad (14)$$

The HCl formed is utilized, with air, for the regeneration of the $CuCl_2$ lixiviant and, in this regard, the use of a cupric chloride system may offer some advantages over the more conventional $FeCl_3$-HCl system. Silver extractions were reported to be 59-86%, and this may reflect either the enhanced attack of silver minerals by cupric ion or simply the fact that easily-leached Ag minerals were present in the concentrates. Overall lead recoveries from concentrate to bullion were >97%. The total impurity problem does not appear

to have been addressed in detail in the Reynolds process, and there are likely difficulties related to the collection, use and recycle of the HCl and H_2 gases. The energy requirements for the high temperature leaching of $PbCl_2$ may not be excessive if good heat exchange/steam recovery is used.

The potential advantage of the low temperature $FeCl_3$ or $CuCl_2$ leach process for lead concentrates is that it tends to be selective for lead, and impurity buildup problems are minimal. The disadvantage of this general approach is that some forms of silver (e.g., tetrahedrite) are not extensively attacked, and that pretreatment or auxiliary leaching steps may be needed (4,5). The low temperature process also suffers in that potential byproduct metals (e.g., Cu, Zn, Bi, etc.) may not be extensively leached and will report to the leach residue, creating both environmental problems and process losses. At this time, the application of the low temperature leaching process for lead concentrates would seem to depend on the nature of the concentrate, but especially on the quantity and leachability of the silver it contains.

PROCESS DEVELOPMENT - HIGH TEMPERATURE PROCESSES

The low temperature leaching process may be well suited to some clean concentrates, but may not be universally applicable, without extensive modification, to all lead feeds. The use of a high-temperature (90-105°C) ferric chloride or cupric chloride leaching process retains most of the strengths of the low temperature route while offering a potential means of treating all lead concentrates regardless of their silver and impurity levels or mineral forms.

The U.S. Bureau of Mines has pioneered the ferric chloride leaching of lead concentrates and has, with industry support, investigated this option at a substantial pilot scale. In the Bureau's process which is summarized

in Figure 3 (10-14), the galena concentrate is leached for a short time at 100°C using a concentrated $FeCl_3$-NaCl medium containing ∿40 g/L Fe^{3+} and 90 g/L Na as NaCl; the pulp density is about 80 g of 68% Pb concentrate per litre. As was the case at lower temperatures, elemental sulphur is the principal sulphidic reaction product.

$$2FeCl_3 + PbS \longrightarrow 2FeCl_2 + PbCl_2 + S^o \qquad (15)$$

For the 0.25-0.50 h leaching period employed, over 99% Pb extraction was realized together with 45% Ag, 30-40% Zn, 20% Cu, 2% Fe, 1-6% Sb and 40% Cd. Clearly a brief high-temperature leach is only partially successful in dissolving silver and longer times would be required for higher silver recoveries, especially if refractory silver minerals were present. The Bureau observed (11) that a 4-h leach period increased the extractions of Ag, Zn, Cd and Cu to 89, 93, 96 and 74%, respectively. Following leaching, the hot slurry is filtered with the leach residue being rejected; $PbCl_2$ is then crystallized by multi-stage vacuum evaporation to ∿40°C (13) and is filtered and dried. High quality lead metal is produced by fused salt electrolysis at 450°C with the evolved chlorine being used to regenerate the leaching medium in a separate operation. Some sulphate enters the system either via sulphates present in the concentrate (e.g., $PbSO_4$, $CaSO_4$) or through minor sulphate formation during the leaching of the sulphide minerals. The Bureau evaluated sulphate control both as sodium jarosite ($NaFe_3(SO_4)_2(OH)_6$) and as gypsum. Jarosite is the preferred option since gypsum tends to report in the $PbCl_2$ crystals and this contamination results in problems during electrolysis; gypsum precipitation was used in the pilot campaigns.

Elemental sulphur contained in the leach residue could be burnt directly for acid manufacture or extracted to yield a pure sulphur product. On a

commercial level, the preferred extractant would appear to be sodium sulphide (15) although ammonium sulphide could also be used (14,16). The use of organic extractants will likely be too costly, and will create environmental problems unless all the organic can be eliminated from the residue. Regardless of the option ultimately selected, some treatment of the sulphur-sulphide leach residue will probably be necessary to prevent the gradual release of acid and heavy metals to the environment by a combination of chemical and bacterial oxidation. The Bureau of Mines has assessed the residue storage component of their process, and have shown that the addition of dolomite (or other alkalinity reagents) controls both the acid and heavy metals (17).

The operation of the Bureau's 500 lb Pb/day pilot plant (Figure 3) has been discussed recently (18,19,19a). All parts of the process worked technically and there is an inherent simplicity in the process. A single-stage leaching step is used and purification is effected through a single crystallization step. The fused salt electrolysis step, although not optimized, functioned well, and only minimal corrosion problems were encountered. Ambient air standards for lead appear to have been met although venting of the tanks was necessary to control lead aerosols. It appears that problems still exist with impurity control, especially as concerns Ag, Cu, Zn and SO_4. Sodium sulphide was later used to precipitate Ag and Cu, and $CaCl_2$ was used to regulate the sulphate level at about 3 g/L. Silver extractions were low and variable (48-80%), in part reflecting the brief 0.25-0.50 h leaching period and in part the complexities of silver mineralization. Uncertainties were also seen (3) in the following areas:

1) Byproduct recovery, especially Ag, Cu, Bi, etc.

2) Design of the fused salt cell, its scaleup, heat balance, etc.

3) Disposal/recycle of contaminated fused salt electrolyte

4) Energy costs associated with the crystallization of the required high-purity $PbCl_2$

5) Chlorine gas recycle and utilization.

The Bureau's process has also been evaluated for low tonnage, high-silver lead concentrates containing up to 2800 ppm Ag (20), and was claimed to be technically and economically attractive. The form of silver in the concentrates evaluated was not given. Economic analysis of the general process, without major silver credits, has suggested the approach is viable for a lead selling price of $0.68/kg.

A process very similar to that of the U.S. Bureau of Mines has been evaluated for two Indian lead concentrates containing 68 and 62% Pb (21). For the low-lead feed, greater than 99% recovery of Pb, Cu and Zn was obtained after 0.5 h of leaching at >100°C with 275 g/L $FeCl_3$, 250 g/L NaCl and 12 g/L HCl. The behaviour of Ag and the methods of impurity control were not discussed. Lead was electrowon from aqueous $PbCl_2$ media with a current efficiency of >98%. This work extends the range of concentrates tested by the Bureau's process and has also confirmed that ferric chloride media result in more rapid oxidation of lead concentrates than ferric sulphate solutions.

Minemet Recherche (22) has also developed a high temperature $FeCl_3$ leach process which is flexible enough to treat either high-grade or off-grade lead concentrates, and their flowsheet is given in Figure 4. The process was tested at various scales and ultimately in a 1 m^3 leach pilot plant operating at about 1 t/d. Leaching was done countercurrently in two stages at 90-100°C using a 25 g/L $FeCl_3$ - 250 g/L NaCl medium; the pulp density appears to be ~30 g/L with an Fe concentration of 10 g/L in excess of the stoichiometric requirement in the first stage of the two-stage leach process. The pulp is subjected to counter current washing prior to discharge whereas the lead-rich

solution is clarified hot prior to purification. Two stages of purification are used. In the first, lead powder is added to precipitate Cu, Ag, Bi, etc.; any traces of unreduced Fe^{3+} ion will also be consumed by the lead. In the second stage, the solution is treated by an ion exchange process, using resin IMACTI-G173, to eliminate the last traces of Ag and Cu and thereby allow the production of 99.99% Pb. Because of the low pulp density and high NaCl content, $PbCl_2$ does not crystallize from the solution, and is actually recovered continuously by electrolysis at 85°C from the aqueous, iron-bearing leaching medium. The electrolysis is conducted in a diaphragm cell using graphite anodes and Ti cathodes; lead metal forms as a powder which falls from the cathode, is collected continuously and is ultimately melted. The ferric chloride leaching solution is regenerated in the anode compartment thereby eliminating the need for chlorine collection and handling with a corresponding 0.6 V reduction in the anode voltage.

$$Pb^{2+} + 2e \longrightarrow Pb^{o} \qquad (15)$$

$$2Fe^{2+} - 2^{e} \longrightarrow 2Fe^{3+} \qquad (16)$$

Zinc dissolution poses some problems in the Minemet process, and it is proposed to control this either by a two-stage sulphide precipitation or by IX-SX methods. With the above process, lead recoveries to bullion exceeded 97% for conventional concentrates and 92% for low-grade bulk concentrates. Silver recoveries were erratic at 19-85%, reflecting the importance of the silver mineralization.

The use of aqueous electrolysis for lead recovery offers several advantages, including:

1) A lower energy requirement per unit of lead
2) Greater opportunities for solution purification
3) Ease of scaleup because of existing knowledge of aqueous electrolysis

4) The potential to regenerate the $FeCl_3$ leaching medium without a separate chlorination step

5) Greater ease of temperature control/heat balance.

Both Minemet (22) and the Bureau of Mines (23) have examined aqueous electrolysis. Workers at the latter establishment indicated energy requirements of ∿0.67 kWh/kg for the aqueous route versus ∿1.32 kWh/kg for fused salt electrolysis. The chief impediment to the aqueous route is seen to be the formation of dendrites or powder rather than a compact lead plate although industry seems quite willing to handle metal powders if they separate readily from the cathode. The production of compact lead layers (likely related to the need for higher $PbCl_2$ solubilities) would clearly tip the scales in favour of the aqueous process.

CANMET is also examining the hot (∿100°C) ferric chloride leaching of both Zn-Pb-Cu-Ag bulk concentrate and various Pb concentrates (24), and a tentative flowsheet for this process is indicated in Figure 5. The lead concentrate is leached at 100°C in $FeCl_3$-NaCl brine to solubilize both the lead and silver as chlorides. Chlorine gas may be sparged into the leaching tanks. Because of the refractory nature of many silver minerals, leaching times as long as 5 h are employed with the objective of dissolving all the metal values. Following hot filtration, the solution is treated with Pb and/or Cu powder to reduce the levels of Ag and Cu <1 ppm. Crystals of $PbCl_2$ are then formed by cooling the solution. The spent leach liquor is next treated by solvent extraction to remove zinc which is eventually recovered as a $ZnCl_2$ solution and is electrolyzed to give a compact zinc deposit and chlorine gas. The spent solution is then partially oxidized with air both to regenerate some of the $FeCl_3$ but mostly to precipitate excess iron; the remaining $FeCl_3$ is regenerated utilizing the chlorine made during the

electrolysis of the zinc and lead chlorides. Lead recovery is by molten salt electrolysis although the aqueous route is also being investigated. The CANMET process has not yet been run in an integrated manner, but various parts of the process have been examined in some detail.

Dissolved silver chloride has been found to react rapidly with either lead or copper powders; copper can be readily cemented from chloride media by lead powder (25,26). The cementation rates were insensitive to temperatures >70°C and stirring speeds >1250 rpm. It was found that the iron-bearing solutions had to be pretreated with granular lead to reduce traces of Fe^{3+} which caused re-dissolution of the Cu or Ag. A neutral atmosphere was employed after pretreatment to prevent air oxidation of the solution. In general, the cementation rates were rapid and both silver and copper could be reduced to <1 ppm using copper powder to remove silver, followed by lead powder for copper elimination. It is proposed to conduct the silver cementation on the hot pregnant solution to avoid any possible contamination of the $PbCl_2$ crystals with AgCl. Separate solubility measurements have shown that high AgCl solubilities (>2 g AgCl/L) are encountered in hot media, but that these fall to low values (50-500 mg/L) in cold solution. The co-precipitation of AgCl with $PbCl_2$ does not seem to have been investigated. The solubility measurements have also clarified the effect of $ZnCl_2$ on the solubility of AgCl in concentrated chloride media. The $ZnCl_2$ has a slight effect on the AgCl solubility causing it to fall for increasing concentrations to about 2 M $ZnCl_2$ and thereafter to rise gradually. In general for other salts, increasing chloride concentrations and temperatures enhance the AgCl solubility.

Sulphate control during the leaching operation is difficult to effect without causing some sulphate contamination of the $PbCl_2$ crystals. Three

methods of SO_4 control are under study; viz., gypsum, K-jarosite and barium sulphate. Although gypsum precipitation by $CaCl_2$ addition can be used to regulate the SO_4 content at a modest level, some SO_4 reports to the $PbCl_2$ crystals, likely because of the slow precipitation of $CaSO_4$ during cooling. Potassium jarosite ($KFe_3(SO_4)_2(OH)_6$) formed by the addition of KCl to the leaching medium also can regulate the SO_4 level at a modest concentration, but some potassium contamination of the $PbCl_2$ crystals is evident. Close control of the free acidity is required, furthermore, to achieve any significant degree of sulphate precipitation (27). Sub-stoichiometric additions of $BaCl_2$ to the leaching medium can effectively precipitate SO_4, but excess $BaCl_2$ resulted in precipitation of $BaSO_4$ in the $PbCl_2$ crystals and, of course, $BaCl_2$ is comparatively expensive.

Because Pb and Zn are often intimately associated in concentrates, the elimination of Zn from the lead processing circuit is important. This step is, however, comparatively difficult if the concentrate contains large amounts of zinc and if a hot $FeCl_3$ leaching process is employed. Because of the long times and >100°C temperatures used to enhance silver recovery, virtually all the zinc contained in the concentrate is leached and, at some point, must be eliminated from the circuit. In the CANMET process, zinc is solvent extracted from a bleed stream by 60% TBP in Solvesso 150 aromatic diluent (28,29). A strip solution containing 15 g Zn/L at pH 1.0 is produced, and this is suitable for zinc electrolysis. Other impurities in the circuit are controlled either by precipitation with the leach residue (Figure 5) or by cementation. The electrolytic recovery of Zn from a $ZnCl_2$ solution seems feasible with smooth, compact, dendrite-free zinc deposits having been obtained on a small pilot scale (30,31,32). The key to the production of smooth deposits is good solution agitation which, in this instance, is effected by air sparging.

Tetrabutylammonium chloride at the 15 mg/L level was found to be the best of the tested levelling agents. Impurity control was no more difficult than for conventional zinc sulphate electrolysis, and current efficiencies and energy requirements were at least as good.

Although CANMET has not developed a fused salt cell for lead electrolysis, considerable background work has been done to assist with the design of such a cell. The limited amount of relevant literature on the electrolysis of $PbCl_2$ in molten salt systems has been surveyed (33). Calculated phase diagrams and vapour pressure curves have been produced (34), and it is clear that several systems are potentially useful; viz., NaCl-$PbCl_2$, KCl-LiCl-$PbCl_2$, NaCl-LiCl-$PbCl_2$ and KCl-NaCl-$PbCl_2$. Current efforts favour a non-lithium system for cost reasons and for general compatability with the leaching circuit. Use of the KCl-NaCl-$PbCl_2$ system seems attractive with the KCl being necessary for sulphate control as jarosite. Densities of the molten salt systems have been measured (35) and the surface tensions have been determined (36,37). Extensive creeping of all the electrolytes is anticipated, especially in the presence of oxygen. Electrical conductivities will soon be reported. The partitioning of impurities between the lead bullion, molten salt bath and vapour phase has been elucidated and the effect of the impurities on the current efficiency for $PbCl_2$ electrolysis has been ascertained (38). Silver reports to the bullion together with about 25% of the copper. Bismuth also reports to the bullion but the extent depends on the Bi concentration of the molten salt bath. Both Cu and Fe caused significant reductions in the current efficiency for lead deposition.

In most of the chloride leaching processes described above, chlorine gas is formed during metal electrolysis and is used to regenerate the $FeCl_3$ lixiviant. Several attempts have been made to circumvent a separate iron

regeneration step by injecting the chlorine gas directly into the concentrate leaching circuit. Pool et al. (39) described the pilot-scale processing of a Cu-rich lead matte containing 52% Pb and 20% Cu. Chlorine gas was injected into an acidified slurry at 90-106°C to convert lead to the chloride; next, oxygen at 48 psi was introduced into the acidic solution to oxidize the other metals.

$$PbS + Cl_2 \longrightarrow PbCl_2 + S^o \qquad (17)$$

$$MS + 2HCl + \tfrac{1}{2}O_2 \longrightarrow MCl_2 + H_2O + S^o \qquad (18)$$

The slurry was cooled and filtered; copper was recovered by solvent extraction and a $PbCl_2$ product was recuperated by brine leaching the residue. Eventually, lead was produced by fused salt electrolysis with an overall recovery of 96% as a 99.99% Pb product. Elemental sulphur was the principal sulphidic species but the Eh of the chlorine leach would have to be carefully controlled to prevent excessive sulphate formation. Data on Ag deportment were not presented.

Akzo Zout Chemie (40) is reportedly examining a somewhat similar process involving Cl_2 injection into hot $CaCl_2$ brines; the Cl_2 gas is reported to dissolve the silver which is eventually recovered by cementation. Presumably lead chloride formed by cooling the solution would be electrolyzed to yield bullion and Cl_2 gas for recycle to the leaching stage. Further details on this process are not available.

PROCESS DEVELOPMENT - ELECTROLEACHING PROCESSES

Various efforts have also been made to combine the leaching and electrolysis steps into one operation to avoid the release, collection and handling of Cl_2 gas altogether. Kammel (41,42) investigated the electroleaching of PbS

slurries to form lead metal and elemental sulphur. Most recently, the Dextec process has evaluated the electroleaching of Pb-Cu concentrates at 90°C in 250 g/L NaCl solution using various diaphragm cells (43). A schematic flowsheet of the process is given in Figure 6. Lead is selectively leached and is eventually recovered as lead powder with an energy requirement of only 0.6 kWh/kg. Copper is also recovered electrolytically and the silver would likely be co-electrolyzed. The proposed reactions are

anodic: $PbS + 2H^+ \longrightarrow Pb^{2+} + H_2S$ (19)

$H_2S \longrightarrow S^o + 2H^+ + 2e^-$ (20)

cathodic: $Pb^{2+} \longrightarrow Pb^o + 2e^-$ (21)

Although the efforts of Kammel and the Dextec workers have materially advanced the concept of direct sulphide electrodissolution, it seems that much work still remains to be done in the areas of diaphragm life and operation, impurity control and, especially, cell design. At this stage of development, it still seems desirable to separate the leaching step from the metal recovery operation. Although this imposes extra processing steps, it simplifies operations and permits purification of the solutions/precipitates with the aim of producing high-purity lead and various byproducts such as silver.

PROCESS DEVELOPMENT - LOW TEMPERATURE CHLORINATION

Some effort has also been expended to replace the $FeCl_3$ leach component of the process with a low temperature chlorination process. This offers the potential advantage of complete conversion of all sulphides, including silver, into chloride form. The chlorination step would have to be done at a low enough temperature (<500°C) to prevent excessive volatilization of some

values and, presumably, some degree of impurity rejection could be achieved by selective leaching of the product chlorides.

Early exploratory work by the U.S. Bureau of Mines (44) indicated that galena concentrates could be readily chlorinated at temperatures above 250°C. The concentrates were pelletized using molasses as a binder, dried and then chlorinated for 45 min. By finishing the reaction >450°C, sulphur contents of the chlorinated product were 0.2-2.4%. By increasing the chlorination temperature to ~600°C, further reductions in the sulphur levels were achieved and some volatilization of impurities occurred. The chlorinated melt was electrolyzed directly without any subsequent purification and, of course, this resulted in the eventual contamination of both the bath and the bullion, especially by zinc and copper. It was established that pure $PbCl_2$ was a most unsatisfactory electrolyte and recourse was made to $PbCl_2$-$CaCl_2$ melts. Silver was shown to be totally (>99%) chlorinated and to report selectively to the lead bullion during electrolysis. Only batch, small-scale, short-time testwork was done, but it was established firstly that >99% chlorination of Pb and Ag was possible at <600°C and secondly that some form of purification would be required for sustained electrolytic operation.

Cyprus Metallurgical Processes Corp. and Hazen Research (45) reported extensively on their fused salt cell design as part of a dry chlorination route to lead. Lead chloride was prepared by leaching the chlorinator product in 300 g/L NaCl at pH 1.5 and 95-100°C; pure $PbCl_2$ was formed on cooling during two-stages and this represents a significant improvement over the Bureau's exploratory work. Lead was recovered in a 2,000 A cell employing a lead pool cathode and vertical carbon plate anodes. A $PbCl_2$ (90%) - NaCl (10%) electrolyte at 500°C was used and the feed rate of Pb was 5.2 kg/h. With this arrangement, Pb and Ag extractions both exceeded 99%. Some problems

were encountered with low current efficiencies, supposedly caused by the buildup of iron in the molten bath. This problem could be resolved by returning the contaminated salt to the brine leach stage. In this process, silver was recovered by cementation on lead from the cooled brine leach solution although hot cementation might be required if significant silver values were present. Fused salt electrolysis was reported to require 1.2 kWh/kg of lead produced.

A somewhat similar process was advocated at UOP Inc. (46,47). In their process, the lead concentrate was reacted with air and chlorine gas at 80-120°C to effect >95% $PbCl_2$ formation while chlorinating only 3% Zn, 9% Fe and 1% Cu. The behaviour of Ag was not considered. The chlorinated product was brine leached in 300 g/L NaCl solution at ~100°C and the slurry was then filtered hot. Lead chloride crystals were produced by cooling the brine, but these had the following composition:

Sb	-	100 ppm
As	-	100 ppm
Bi	-	80 ppm
Fe	-	70 ppm
Zn	-	30 ppm
Cu	-	20 ppm
Ag	-	20 ppm

Clearly, even the low temperature chlorination route coupled with brine leaching - $PbCl_2$ crystallization is inadequate to produce a high purity feed for the electrolysis step which was done at 550°C in a 92% $PbCl_2$ - 8% NaCl bath. Silver and copper could be reduced to 3 and 11 ppm, respectively, by cementation for 25 min on Pb powder at 75°C. Iron control by the goethite process was used to keep the Fe content of the circulating brine at <0.8 g/L. Detailed data on the control of other impurity elements were not presented.

FUNDAMENTAL CONSIDERATIONS

Despite the number of chloride leaching processes advanced for lead concentrates, very few systematic studies of the ferric chloride and/or cupric chloride leaching of galena have been reported. Dutrizac and MacDonald (48) summarized the early work on this subject and their conclusions are:

1 - Ferric chloride is more effective than ferric sulphate for leaching lead concentrates

2 - $FeCl_3$ leaching rates are rapid, but the rate decreases (parabolically?) with time because of the formation of a sulphur layer

3 - Elemental sulphur is the principal sulphidic reaction product.

Peters (49) likewise noted the comparative lack of definitive information on the fundamentals of galena leaching, and showed that the formation of elemental sulphur in acid media was consistent with the Eh-pH diagram for the Pb-S-H_2O system. Paramguru et al. (50) studied the dissolution of a low grade lead ore in ferric chloride media and found that maximum lead extractions occurred for a 2.5X excess of $FeCl_3$. Also, their apparent activation energy was 13.8 kJ/mole (3.3 kcal/mole), but this seems to be too low a value for the galena dissolution reaction. Their results were clearly influenced by the presence of significant amounts of impurities in the ore, and their data should not be related to relatively pure galena.

Kinetically informative studies on relatively pure sized galena have been reported by Arai et al. (51) and by Kim and Kim (52); similar studies on massive galena have been done by Dutrizac (53). Leaching studies in progress at the University of Utah have been cited by Wadsworth (54). The findings of these researchers are compared in Table 1. Although there are points of difference, the agreement among these kinetic studies is fairly good.

Table 1 - Comparison of kinetic data for the ferric chloride leaching of galena

	Arai et al. Ref. 51	Kim and Kim Ref. 52	Dutrizac Ref. 53	Wadsworth Ref. 54
Form of Kinetic Curves	Not linear	Parabolic kinetics	Parabolic kinetics	Parabolic kinetics for any significant degree of dissolution
Principal Sulphidic Reaction Product	S^o, trace SO_4	S^o	S^o, trace SO_4	S^o
Effect of Area	Rate increases directly with area	Parabolic rate increases directly with area	Parabolic rate increases directly with area	-
Effect of $FeCl_3$	Rate increases as $[FeCl_3]^{1.0}$	Rate increases as $[FeCl_3]^{1.2}$; in 3 M NaCl rate increases as $[FeCl_3]^{2.2}$	For 0.1 M $FeCl_3$, rate increases as $[FeCl_3]^2$. For $FeCl_3$ >0.1 M rate decreases slightly with increasing $FeCl_3$.	Rate increases as $[FeCl_3]^{1.0}$ for $FeCl_3$ <0.2 M and 4 M NaCl
Effect of HCl	No effect below 0.1 M HCl	-	Negligible effect below 1.0 M HCl	-
Activation Energy 0 M NaCl	33-46 kJ/mol	53 kJ/mole	43 kJ/mole	"very modest temperature dependence"
3 M NaCl	-	38 kJ/mole	∿53 kJ/mole	-
Rotation Speed	-	Rate increases with rpm	Rate essentially independent of rpm <1000	
Effect of Chloride Salts	-	Rate increases with NaCl and slightly with $CaCl_2$	Rate increases with NaCl or KCl; slight increase with $CaCl_2$ or LiCl; negligible effect with $FeCl_2$	

There is a consensus that the rates are rapid and generally parabolic, indicative of some form of protective layer formation. The clearly-defined parabolic nature of the leaching curves is shown in Figure 7 for massive galena mounted in plastic and leached under controlled hydrodynamic conditions. The excellent linear agreement on the wt^2 vs time basis clearly indicates parabolic leaching kinetics. Surprisingly, the rate depends slightly on the rotation or stirring speed and is influenced, to various degrees by non-oxidizing chloride salts in solution. The mechanistic interpretation of the results is not yet finalized, but appears to involve the diffusion of some species, possibly the $PbCl_2$ reaction product, through the semi-porous elemental sulphur product layer. That the outward diffusion of $PbCl_2$ is involved is clearly indicated by the data given in Figure 8 where the effect of the initial lead concentration of the bulk solution on the parabolic rate constant for galena dissolution is presented. If it is assumed that a nearly saturated $PbCl_2$ solution is produced adjacent to the reacting surface of the galena, then the diffusion gradient (G) for lead becomes:

$$G = \frac{(PbCl_2)_{saturated} - (PbCl_2)_{bulk\ solution}}{d} \qquad (22)$$

where d is the thickness of the porous sulphur layer. If it is further assumed that the outward diffusion of the $PbCl_2$ reaction product controls the galena dissolution rate, then the rate should decrease as the $PbCl_2$ concentration of the bulk solution increases, thereby reducing the diffusion gradient. The data of Figure 8 (which are based on the amount of Fe^{2+} formed because it is nearly impossible to monitor accurately small changes in lead concentration against such high $PbCl_2$ backgrounds) clearly indicate that the rate declines systematically with increasing concentrations of $PbCl_2$

in the bulk solution. Furthermore, the dissolution rate levels off at a low value for $PbCl_2$ concentrations in excess of 8 g/L and on-going work indicates this is about the $PbCl_2$ solubility limit in a 0.3 M $FeCl_3$ - 0.3 M HCl solution at 80°C. Hence, it appears that the leaching of galena is rapid and is controlled by the outward diffusion of the $PbCl_2$ reaction product through the solution trapped in pores in the constantly thickening elemental sulphur product layer.

All interpretation of the $FeCl_3/CuCl_2$ leaching of galena is complicated by the non-oxidative dissolution of the sulphide in the acidic media. In a 0.3 M $FeCl_3$ medium at 80°C, the direct acid attack represents ~20% of the total dissolution for HCl concentrations <1.0 M. In the range 1.0-2.0 M HCl, the contributions are about equal and at still higher acid concentrations the direct acid attack is dominant. Significantly, very high acid concentrations (>2 M HCl) seem to inhibit the rate in $FeCl_3$ media (53). Direct concentrated acid attack of galena to form $PbCl_2$ and H_2S is felt to be commercially attractive (49) and provides the means of producing a saleable sulphur product. Some of the problems involved in developing such a process would include, however:

1 - The need to work in concentrated HCl media

2 - Gas cleaning

3 - Water evaporation with the H_2S

4 - Silver recovery

5 - Total lack of selectivity

6 - Regeneration of the concentrated HCl solutions

7 - Energy considerations associated with evaporative processes

8 - Corrosion difficulties related to the HCl-H_2S vapours.

The fundamental aspects of the HCl attack of galena seem to be well understood. Scott and Nicol (55) summarized the early work in the field and showed the rate to be controlled by the diffusion of $PbCl_2$ and soluble H_2S from the surface of the galena. The rate increased with increasing concentrations of HCl or chloride ion; the apparent activation energy was ~51 kJ/mole (12.3 kcal/mole). For HCl concentrations <1.0, the rate was not diffusion controlled and significantly slower leaching rates were observed. Recently, Awakura et al. (56) and Majima and Awakura (57) have studied the chemically controlled leaching of galena at high rotation speeds and moderate HCl concentrations. They concluded that the rate was chemically controlled and was first order with respect to the activity of HCl. The presence of neutral chlorides accelerated the rate both by increasing the hydrogen activity and by specific adsorption on the galena.

Various electrochemical studies have been carried out to try to elucidate the reactions occurring during the leaching of galena, but these are often of limited use since only the initial stage of leaching (often only a few monolayers of sulphide) is frequently considered. Such initial reactions are often quite dissimilar to those responsible for bulk sulphide dissolution. For example, the work of Eadington (58), which illustrated a pronounced influence of n-p typing on the galena leaching rate, was concerned with the dissolution of only a few monolayers of PbS. It was concluded that the bulk dissolution of galena would be independent of n-p typing despite the importance of this parameter for the very initial stage of leaching.

All workers who have studied the anodic dissolution of galena in acidic chloride media agree that the dissolution reaction at <1 V SHE is given by the following equation.

$$PbS \longrightarrow Pb^{2+} + S^{o} + 2e \qquad (23)$$

At potentials greater than 1 V, lead sulphate is formed and, of course, $PbSO_4$ is always precipitated on the surface in sulphate systems (59). There is a consensus that the reaction is not reversible because of the sluggish reaction of elemental sulphur, and that the dissolution reaction is impeded by various films formed on the surface of the PbS. There is little agreement, however, on the nature of those impeding films or on the dissolution mechanisms involved.

Paul et al. (60) and Nicol et al. (61) noted that very little SO_4 was formed in perchloric acid media (pH <6) but that increasing amounts were produced at higher pH values. They felt that the sulphide passivation was caused by the progressive thickening of the sulphur layer which in turn retarded the release of Pb^{2+} and caused a concomitant rise in pH. The locally high pH results in the precipitation of a basic lead sulphate which inhibits further dissolution. It was shown that the Tafel slopes were not consistent with a two-electron process as suggested by Equation 23, and that two, one-electron processes occurred.

$$PbS \longrightarrow Pb^{2+} + S^{-} + e \qquad (24)$$

$$S^{-} \longrightarrow S^{o} + e \qquad (25)$$

It was calculated that the slope of the Tafel plots should vary between 40 and 120 mV as the concentration of Pb^{2+} varied, and this was verified experimentally. Although the initial reaction was strongly influenced by the semiconducting properties of the PbS, the bulk dissolution of galena was felt to be completely independent of this factor.

Johnson et al. (62) also investigated the dissolution of PbS in perchloric acid media, and they found mostly elemental sulphur formation at 40°C. Electrodes held at constant potential showed a steady drop in current,

reflective of the parabolic kinetics observed during chemical leaching. The reaction was nearly independent of pH in the range 0-3 but was strongly affected by dissolved Pb^{2+}. The activation energy for the anodic reaction was 10-13 kcal/mole. These workers observed variations in the Tafel slope (cf. Ref. 60,61), but offered no explanation for the behaviour. They concluded that the reaction was activation controlled and involved two single-electron reactions.

Although they were primarily interested in the effect of surface alteration on the floatability of galena, Gardner and Woods (63) also investigated the electrodissolution of PbS in perchloric acid media. They confirmed that, in acid media, no sulphate is formed below ~1.05 V SHE; thiosulphate was produced at moderate potentials and intermediate pH values, but no S_2O_3 was seen at pH 1.0. These workers also found the surface to be passivated, and postulated a coverage by plastic sulphur to account for the decline in current with time at constant potential. It was also assumed that the plastic sulphur eventually crystallized thereby becoming less protective, and that the rates increased somewhat once this occurred. The overall dissolution reaction in acidic media yielded Pb^{2+} and S^o, Equation 23.

The above anodic dissolution studies were done in perchloric acid media. Of greater direct relevance to the ferric chloride leaching of galena are the investigations of Ghali and Dandapani (64,65) on the anodic dissolution of synthetic PbS in chloride solutions where the lead ions would experience complexation similar to that seen during ferric chloride leaching. In chloride media, there was clear evidence of passivation caused by the elemental sulphur and/or $PbCl_2$ reaction products.

$$PbS + 2Cl^- \longrightarrow PbCl_2 + S^o + 2e \qquad (26)$$

The ease of anodic dissolution increased with increasing HCl concentrations and the peak in the anodic polarization curves occurred at lower potentials; this was attributed to either a pH or chloride ion effect. Rotation speed exercised little influence on the dissolution reaction, suggesting that mass transfer was not rate limiting. The passivation observed at constant potential (65) was attributed to the coverage of the surface by the reaction products. Sulphur was observed to form in two habits, globular and needle-like, and sulphur alone passivated the surface as noted above (63). When $PbCl_2$ was being produced at a high rate (Equation 26), it formed a uniform amorphous layer on the PbS that severely restricted the dissolution process. At potentials of ∿0.8 V SHE, some $PbSO_4$ was formed according to Equation 27, and this also contributed to the passivation.

$$PbS + 4H_2O \longrightarrow PbSO_4 + 8H^+ + 8e \qquad (27)$$

The anodic studies indicate that the sulphur layer formed will passivate the surface and that the severity of passivation is increased when lead compounds of limited solubility; e.g., $PbCl_2$, $PbSO_4$, etc., are produced. That higher currents are realized in concentrated HCl media suggests that the passivation can be partly controlled by the proper selection of solution composition and leaching conditions.

CONCLUDING REMARKS

Although hydrometallurgical processes for lead have not yet been implemented by the industry, the above discussion indicates that several potentially attractive processes are available in a reasonably advanced state. Although most try to utilize the rapid leaching rates of galena with respect to other sulphides, this may not be an advantage if refractory silver minerals are

present in significant amounts. Bounds (3) suggests that sacrificing high lead or silver recoveries to achieve a limited degree of selectivity will not be economically acceptable. Alternate processes such as electroleaching or low temperature chlorination seem to offer no advantages over a high temperature $FeCl_3$ leach, but present several additional operating problems. Some form of purification beyond that achieved by $PbCl_2$ crystallization is called for, and methods based on cementation or sulphide precipitation seem to offer a basis for success. The most promising means of lead recovery is by electrolysis using either a fused salt or aqueous approach.

Major problems still exist with impurity deportment, and especially with the recovery of silver or gold. None of the processes seems able to achieve consistently >95% Ag recoveries from a variety of feeds. Lead solubilities are low and this means large volumes of solution must be heated and cooled; the need for careful heat conservation is clear. The large number of residues requiring washing suggests that water balance problems will be severe, but this aspect has not received much attention except possibly by Cominco (7,8). Major efforts are required in the design of the electrolytic cells for either aqueous or fused salt electrolysis; the development of smooth lead deposits would greatly simplify design and scaleup of the aqueous tankhouse. Lastly, it should be recognized that the very concept of hydrometallurgical lead processing is being challenged by a new generation of lead flash smelting processes which claim complete SO_2 capture, a clean work place, and the energy efficiency of oxygen smelting.

REFERENCES

1 - Haver, F.P., Uchida, K. and Wong, M.M. "Recovery of lead and sulphur from galena concentrate using a ferric sulphate leach"; RI-7360; U.S. Bureau of Mines; 1970.

2 - Correa, A.A. "Study for obtaining lead from galena concentrates by hydrometallurgy"; Geomimet 107:25-33; 1980.

3 - Bounds, C.O. "Chloride-based lead extraction - Possibly an economic solution to the environmental restraints on lead smelting"; CIM Annual Meeting; April; Toronto; 1980.

4 - Cottam, S.M., Day, H.E. and Griffith, W.A. "Production of lead and silver from their sulphides"; U.S. Patent 3,929,597; December 30, 1975.

5 - Baker, R.D., Cottam, S.M., Day, H.E. and Griffith, W.A. "Method of producing metallic lead and silver from their sulphides"; U.S. Patent 3,961,941; June 8, 1976.

6 - Hamdorf, C.J. "Precipitation of lead and silver from brine solutions by metallic iron"; Proc Australas Inst Min Metal 199:19-50; 1961.

7 - Milner, E.F. and Parker, E.G. "Hydrometallurgical process for treating metal sulphides containing lead sulphide"; U.S. Patent 4,082,629; February 28, 1977.

8 - Anon. "Evaluation of the Cominco hydrometallurgical lead process for the recovery of lead from a pyritic low-grade lead concentrate"; CANMET Contract OSQ76-00129; CANMET, Energy, Mines and Resources Canada; June 1977.

9 - Reynolds, J.E. "Hydrometallurgical process for the recovery of lead"; U.S. Patent 4,276,084; June 30, 1981.

10 - Murphy, J.E., Haver, F.P. and Wong, M.M. "Recovery of lead from galena by a leach electrolysis process"; RI-7913; U.S. Bureau of Mines; 1974.

11 - Haver, F.P. and Wong, M.M. "Ferric chloride-brine leaching of galena concentrate"; RI-8105; U.S. Bureau of Mines; 1976.

12 - Haver, F.P., Elges, C.H., Bixby, D.L. and Wong, M.M. "Recovery of lead from lead chloride by fused-salt electrolysis"; RI-8166; U.S. Bureau of Mines; 1976.

13 - Phillips, T.A. "Economic evaluation of a leach-electrolysis process for recovering lead from galena concentrate"; IC-8773; U.S. Bureau of Mines; 1973.

14 - Haver, F.P., Baker, R.D. and Wong, M.M. "Improvements in ferric chloride leaching of chalcopyrite concentrate"; RI-8007; U.S. Bureau of Mines; 1975.

15 - Lei, K.P.V., Carnahan, T.G. and Eisele, J.A. "Recovery of sulphur and accessory metals from a leaching process residue"; RI-8733; U.S. Bureau of Mines; 1982.

16 - Narain, K.A. "Recovery of elemental sulphur and metal values from tailings from copper recovery processes"; U.S. Patent 4,138,248; February 6, 1979.

17 - Carnahan, T.G. and Lucas, M.A. "Weathering of a base metal sulphide leaching residue"; RI-8667; U.S. Bureau of Mines; 1982.

18 - Wong, M.M., Haver, F.P. and Sandberg, R.G. "Ferric chloride leach-electrolysis process for production of lead"; Lead-Zinc-Tin '80, TMS-AIME; edited by J.M. Cigan, T.S. Mackey and T.J. O'Keefe; Warrendale, Pennsylvania; 445-454; 1979.

19 - Sandberg, R.G. and Wong, M.M. "Technical feasibility study of ferric chloride leaching/electrolysis process for lead metal"; A.I.Ch.E. Symp Ser 78:216:138-142; 1982.

19a - Wong, M.M., Sandberg, R.G., Elges, C.H. and Fleck, D.C. "Integrated operation of ferric chloride leaching, molten salt electrolysis process for production of lead"; RI-8770; U.S. Bureau of Mines; 1983.

20 - Anon. "Hydromet may free small lead districts from the smelter"; Mining Eng 2:147-149; 1979.

21 - Sinha, P.K., Basu, G., Aush, S.C., Dhananjayan, N. and Altekar, V.A. "Recovery of non-ferrous metals and elemental sulphur by ferric chloride leaching of sulphide concentrates"; Trans Indian Inst Metal 33:6:431-438; 1980.

22 - Demarthe, J.M. and Georgeaux, A. "Hydrometallurgical treatment of lead concentrates"; Lead-Zinc-Tin '80, TMS-AIME; edited by J.M. Cigan, T.S. Mackey and T.J. O'Keefe; Warrendale, Pennsylvania; 426-444; 1979.

23 - Haver, F.P., Bixby, D.L. and Wong, M.M. "Aqueous electrolysis of lead chloride"; RI-8276; U.S. Bureau of Mines; 1978.

24 - Dutrizac, J.E. "The leaching of a pyritic Zn-Pb-Cu-Ag bulk concentrate in ferric chloride media"; Division Report MRP/MSL 81-58 (TR); CANMET, Energy, Mines and Resources Canada; 1981.

25 - MacKinnon, D.J. and Brannen, J.M. "Silver cementation on copper, lead and zinc from chloride solutions"; Division Report MRP/MSL 82-117 (TR); CANMET, Energy, Mines and Resources Canada; 1982.

26 - MacKinnon, D.J. and Brannen, J.M. "Silver cementation on copper and lead from chloride solutions"; to be published.

27 - Dutrizac, J.E. "Jarosite formation in chloride media"; Proc Australas Inst Min Metal 278:23-32; 1981.

28 - Ritcey, G.M., Lucas, B.H. and Price, K.T. "Evaluation and selection of extractants for the separation of copper and zinc from chloride leach liquor"; Hydrometal 8:197-222; 1982.

29 - Ritcey, G.M., Lucas, B.H. and Price, K.T. "Extraction of copper and zinc from chloride leach liquors resulting from chlorination roast-leach of fine grained sulphides"; Proc Inter Solvent Extr Conf, ISEC '80; Liege, Belgium; Vol. 3, paper 30-71; 1980.

30 - MacKinnon, D.J., Brannen, J.M. and Morrison, R.M. "Zinc electrowinning from aqueous chloride electrolyte"; J Appl Electrochem 12:39-53; 1982.

31 - MacKinnon, D.J., Brannen, J.M. and Morrison, R.M. "Aspects of zinc electrowinning from aqueous chloride electrolyte"; Chloride Electro-metallurgy, TMS-AIME; edited by P.D. Parker; New York; 1-19; 1982.

32 - MacKinnon, D.J. "The electrowinning of metals from aqueous chloride"; Hydrometallurgy, Research, Development and Plant Practice, TMS-AIME; edited by K. Osseo-Asare and J.D. Miller; New York; 659-677; 1982.

33 - Skeaff, J.M. "Electrowinning of aluminum, magnesium, lead and zinc from molten-chloride electrolytes: A review"; Trans I.M.M. 89:C71-C82; 1980.

34 - Skeaff, J.M., Bale, C.W., Pelton, A.D. and Thompson, W.T. "Selection of ternary fused chlorides for the electrowinning of lead and zinc based on calculated thermodynamic properties"; CANMET Report 79-23; CANMET, Energy, Mines and Resources Canada; 1979.

35 - Gutierrez, A. and Toguri, J.M. "Densities and molar volumes of the $PbCl_2$-KCl-NaCl and $PbCl_2$-KCl-LiCl ternary systems"; J Chem and Eng Data 27:109-113; 1982.

36 - Fujisawa, T. and Toguri, J.M. "Surface tensions of the $PbCl_2$-KCl-NaCl and $PbCl_2$-KCl-LiCl ternary systems"; to be published.

37 - Utigard, T. and Toguri, J.M. "Contact angle measurements of the $PbCl_2$-KCl-NaCl and $PbCl_2$-KCl-LiCl ternary systems by X-ray radiographic techniques"; to be published.

38 - MacKinnon, D.J., Brannen, J.M. and Skeaff, J.M. "The partitioning of impurities during lead electrowinning from molten chloride electrolyte"; Division Report MRP/MSL 82-135 (TR); CANMET, Energy, Mines and Resources Canada; 1982.

39 - Pool, D.L., Scheiner, B.J. and Hill, S.D. "Recovery of metal values from lead smelter matte by chlorine-oxygen leaching"; RI-8615; U.S. Bureau of Mines; 1981.

40 - Miedema, A. Akzo Zout Chemie Nederland bv; personal communication; 1979.

41 - Kammel, R. and Nilmen, F. "Concerning the extraction of lead and sulphur from lead sulphide suspensions in aqueous electrolytes"; Erzmetall 39:9:389-395; 1979.

42 - Kammel, R., Atlam, A., Lieber, H.W. and Nilmen, F. "Electrolytic winning of lead from sulphide raw materials"; Metall 33J:925-933; 1979.

43 - Everett, P.K. "The Dextec lead process"; Hydrometallurgy, Research, Development and Plant Practice, TMS-AIME; edited by K. Osseo-Asare and J.D. Miller; New York; 165-173; 1982.

44 - Starliper, A.G. and Kenworthy, H. "Recovery of lead and sulphur by combined chlorination and electrolysis of galena"; RI-6554; U.S. Bureau of Mines; 1964.

45 - Reynolds, J.E., Goens, D.N. and Kenney, C.W. "Pilot plant development of chloride processes for lead-zinc concentrates"; Lead-Zinc Update, SME-AIME; edited by D.O. Rausch, F.M. Stephens and B.C. Mariacher; New York; 301-325; 1977.

46 - Um, R.T., Tolley, W.K. and Stauter, J.C. "The recovery of lead from sulphide concentrates using a chlorination/brine leach/electrolysis process"; Process Fundam Consid Sel Hydrometall Syst, SME-AIME; edited by M.C. Kuhn; New York; 109-113; 1981.

47 - Stauter, J.C. and Tolley, W.K. "Production of metallic lead"; U.S. Patent 4,149,947; April 17, 1979.

48 - Dutrizac, J.E. and MacDonald, R.J.C. "Ferric ion as a leaching medium"; Minerals Sci Engng 6:2:59-100; 1974.

49 - Peters, E. "Direct leaching of sulphides: Chemistry and applications"; Metal Trans 7B:505-517; 1976.

50 - Paramguru, R.K., Rao, P.K. and Jena, P.K. "Extraction of lead from galena through ferric chloride leaching"; Trans Ind Inst Metal 31:1: 30-33; 1978.

51 - Arai, K., Majima, H. and Izaki, T. "Effect of thermal treatment on the leaching rate of galena in acidic ferric chloride solutions"; Nippon Kogyo Kaishi 95:1096:359-363; 1979.

52 - Kim, S.S. and Kim, I.B. "Leaching of galena with chloride aqueous solutions"; Taehan Kumsok Hakhoe Chi 18:6:586-592; 1980.

53 - Dutrizac, J.E. "Kinetics of galena dissolution in ferric chloride media"; to be published.

54 - Wadsworth, M.E. "Heterogeneous rate processes in the leaching of base metal sulphides"; NATO Advanced Research Institute on Hydrometallurgical Process Fundamentals; Cambridge; July, 1982.

55 - Scott, P.D. and Nicol, M.J. "Kinetics of non-oxidative dissolution of galena in acidic chloride solutions"; Trans I.M.M. 1976:1:C40-C44; 1976.

56 - Awakura, Y., Kamel, S. and Majima, H. "A kinetic study of nonoxidative dissolution of galena in aqueous acid solution"; Metal Trans 11B: 377-381; 1980.

57 - Majima, H. and Awakura, Y. "Measurement of the activity of electrolytes and the application of activity to hydrometallurgical studies"; Metal Trans 12B:141-147; 1981.

58 - Eadington, P. "Leaching of illuminated lead sulphide with nitric acid as a function of the solid-state electronic properties"; Trans I.M.M. C158-C161; 1973.

59 - Iwai, M. "Effect of halogen ions on the anodic dissolution of galena in sulphuric acid solution"; Nippon Kinzoku Gakkaishi 39:3:268-273; 1975.

60 - Paul, R.L., Nicol, M.J., Diggle, J.W. and Saunders, A.P. "The electrochemical behaviour of galena (lead sulphide) - I. Anodic dissolution"; Electrochimica Acta 23:625-633; 1978.

61 - Nicol, M.J., Paul, R.L. and Diggle, J.W. "The electrochemical behaviour of galena (lead sulphide) - II. Cathodic reduction"; Electrochimica Acta 23:635-639; 1978.

62 - Johnson, J.W., Chang, J., Narasagondar, R.A. and O'Keefe, T.J. "Anodic dissolution of galena concentrate in perchloric acid"; J Appl Electrochem 8:25-32; 1978.

63 - Gardner, J.R. and Woods, R. "A study of the surface oxidation of galena using cyclic voltammetry"; J Electroanal Chim 100:447-459; 1979.

64 - Ghali, E. and Dandapani, B. "Anodic behaviour of lead sulphide in hydrochloric acid"; J Appl Electrochem 10:335-344; 1980.

65 - Dandapani, B. and Ghali, E. "The nature of passivation of lead sulphide during anodic dissolution in hydrochloric acid"; J Electrochem Soc 129:2:271-276; 1982.

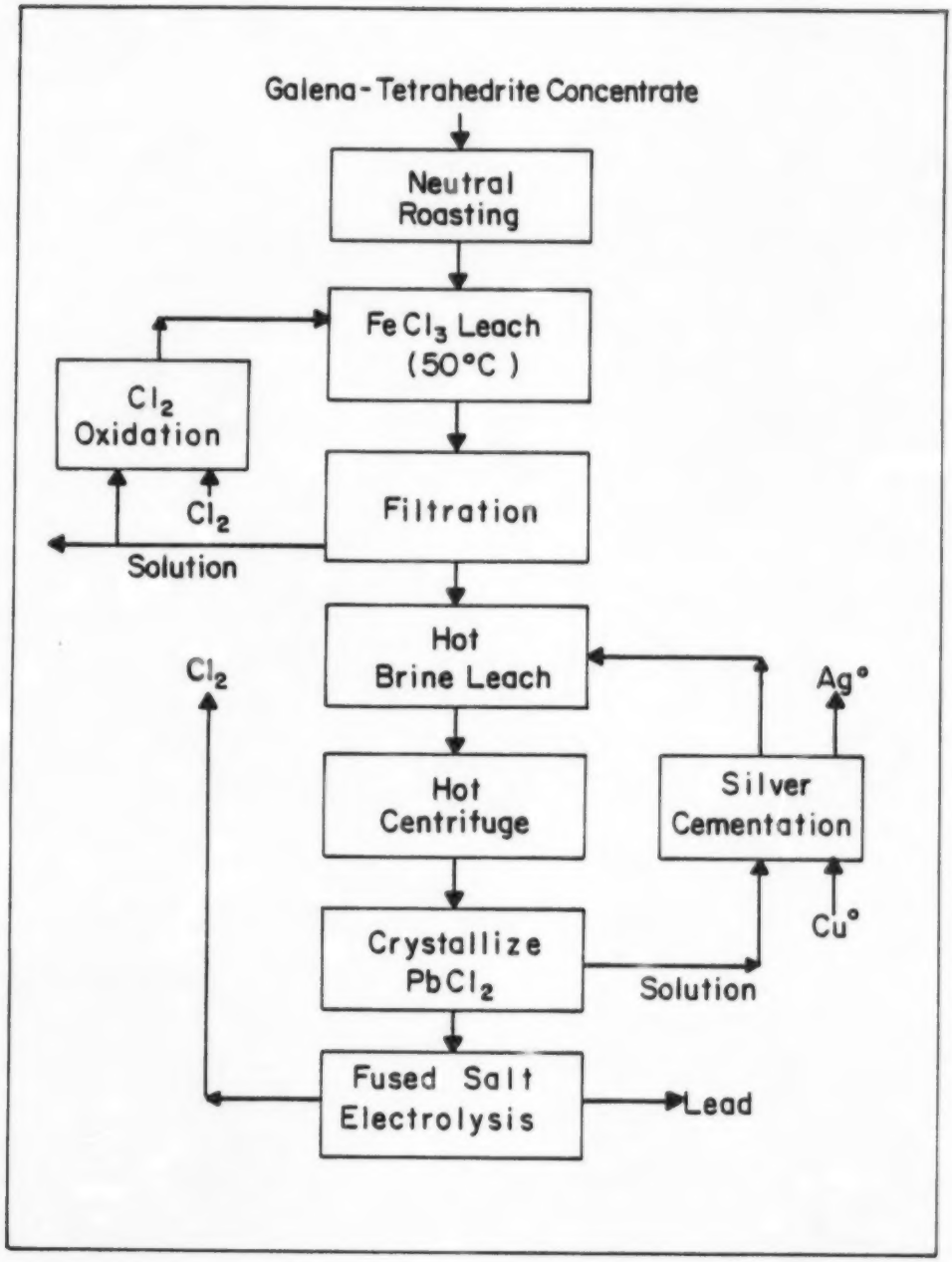

Fig. 1 - Hecla Mining Company ferric chloride leach process for Pb-Ag concentrates that incorporates the neutral roast option. Ref. 4,5.

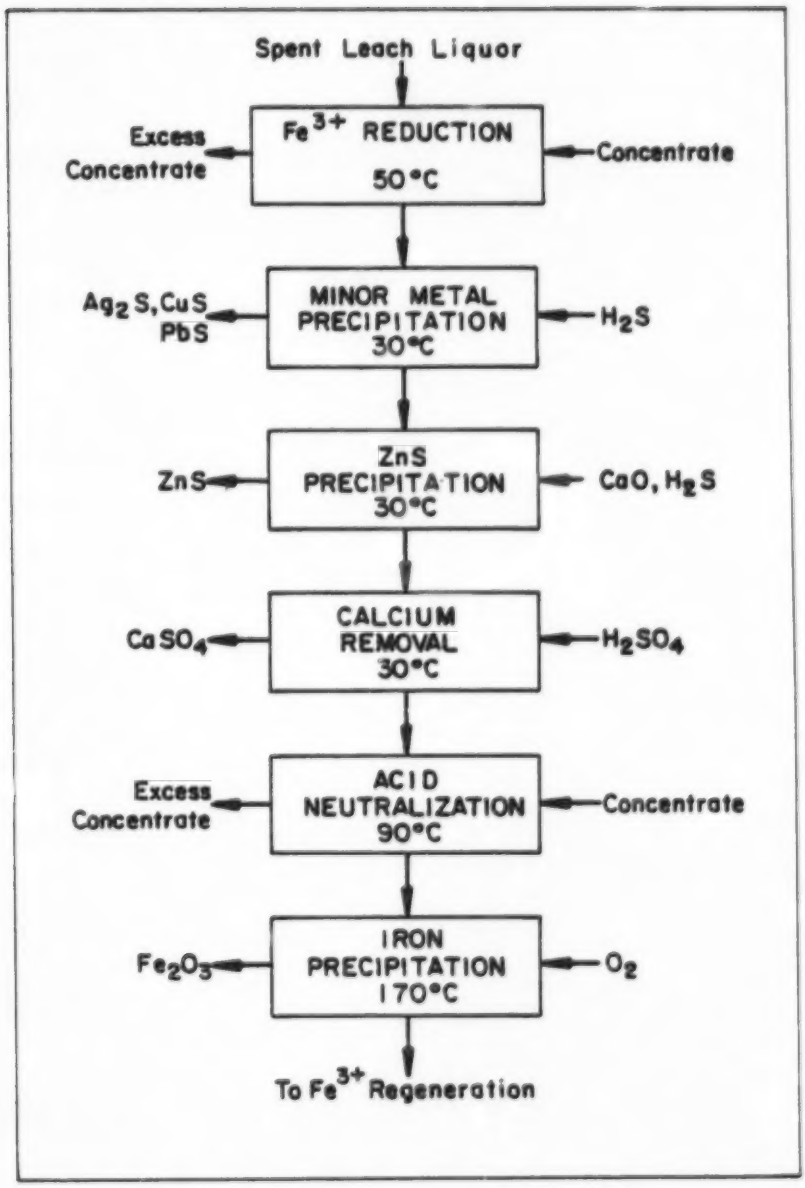

Fig. 2 - Cominco flowsheet for the solution purification stage of their ferric chloride leach process for lead concentrates. Ref. 7,8.

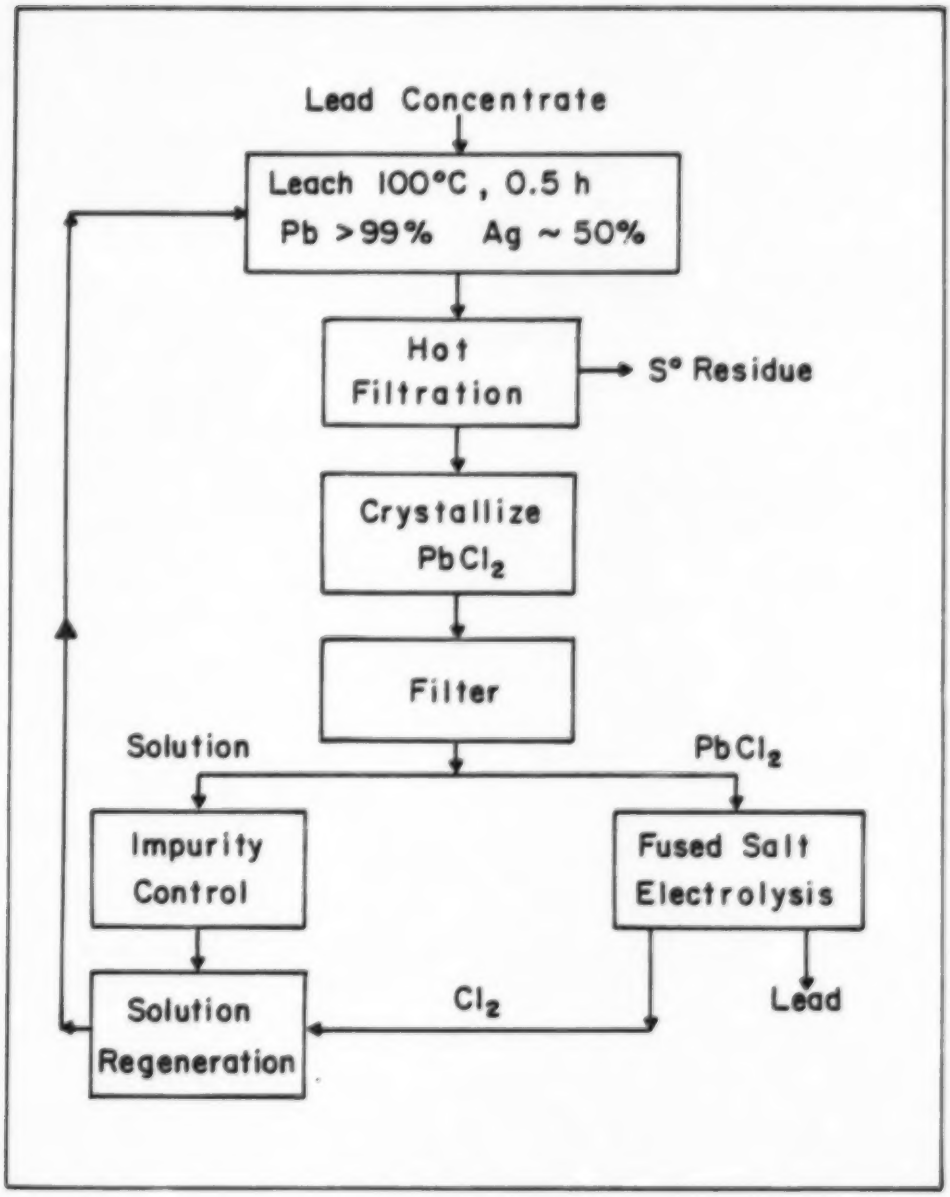

Fig. 3 - Schematic flowsheet of the U.S. Bureau of Mines process for lead concentrates that was tested at a 500 lb Pb/day scale. Ref. 18, 19,19a.

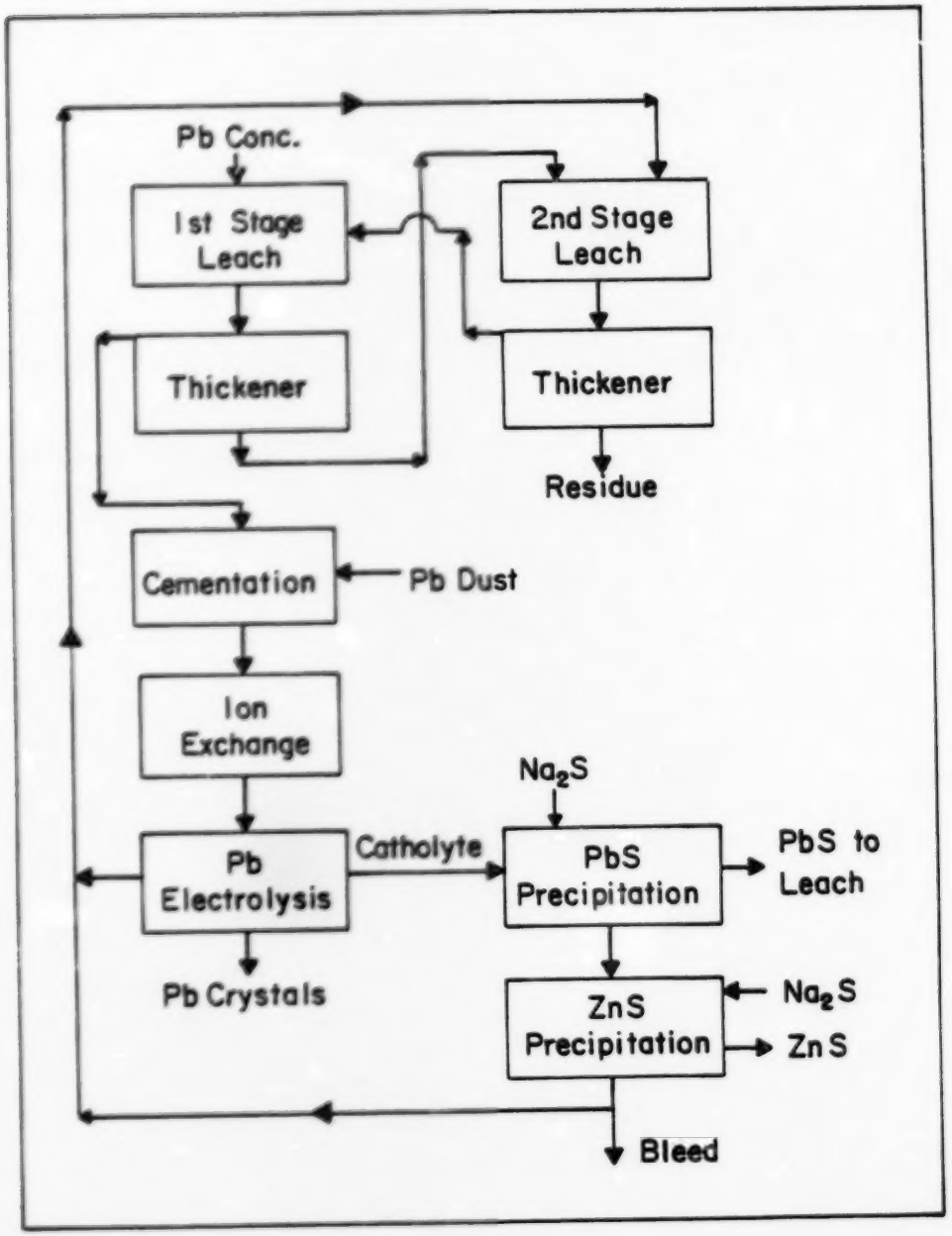

Fig. 4 - Flowsheet of the Minemet ferric chloride leach process for lead concentrates. Ref. 22.

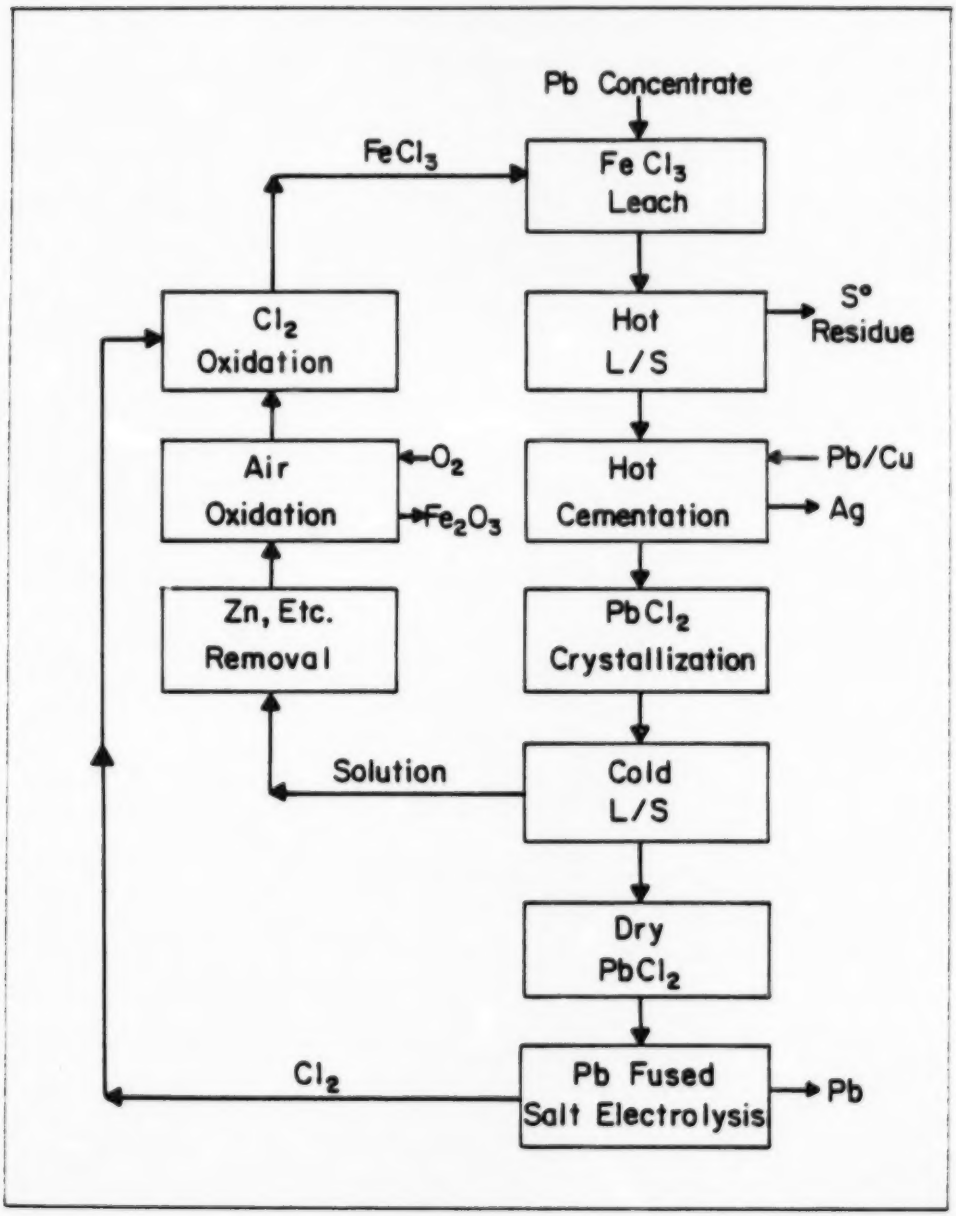

Fig. 5 - Tentative flowsheet of CANMET's ferric chloride leaching process for lead concentrates. Ref. 24.

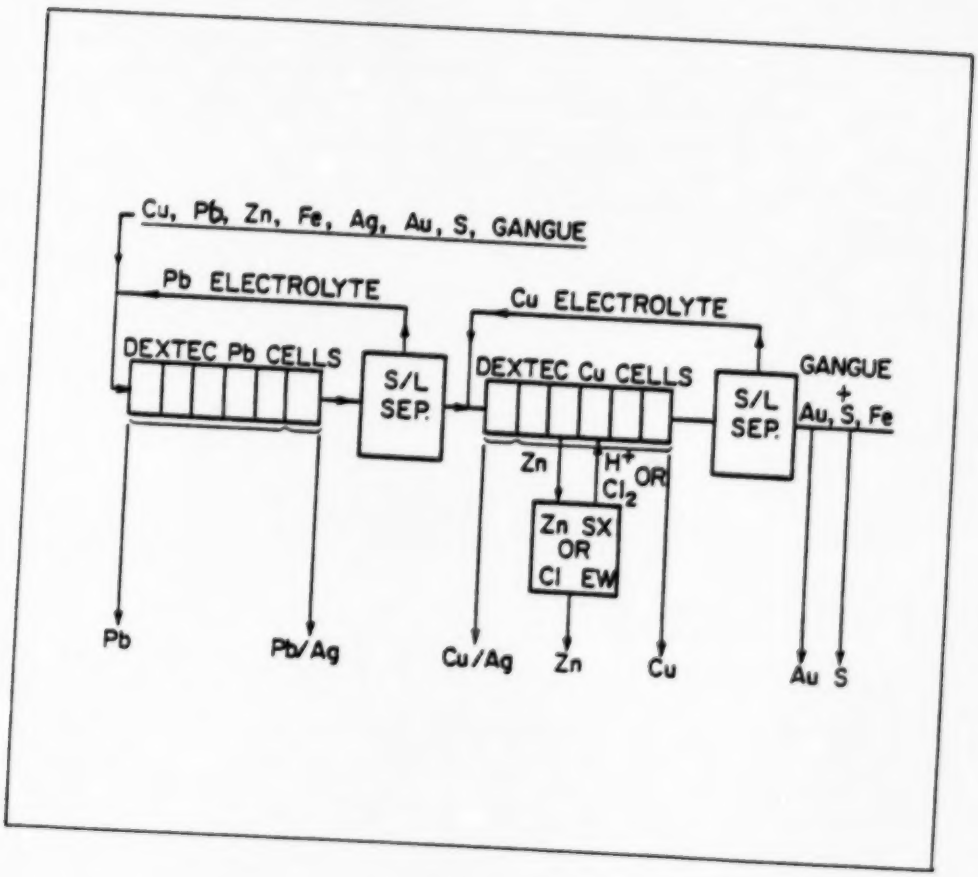

Fig. 6 - Flowsheet of the Dextec electroleach process for Pb-Cu concentrates. Ref. 43.

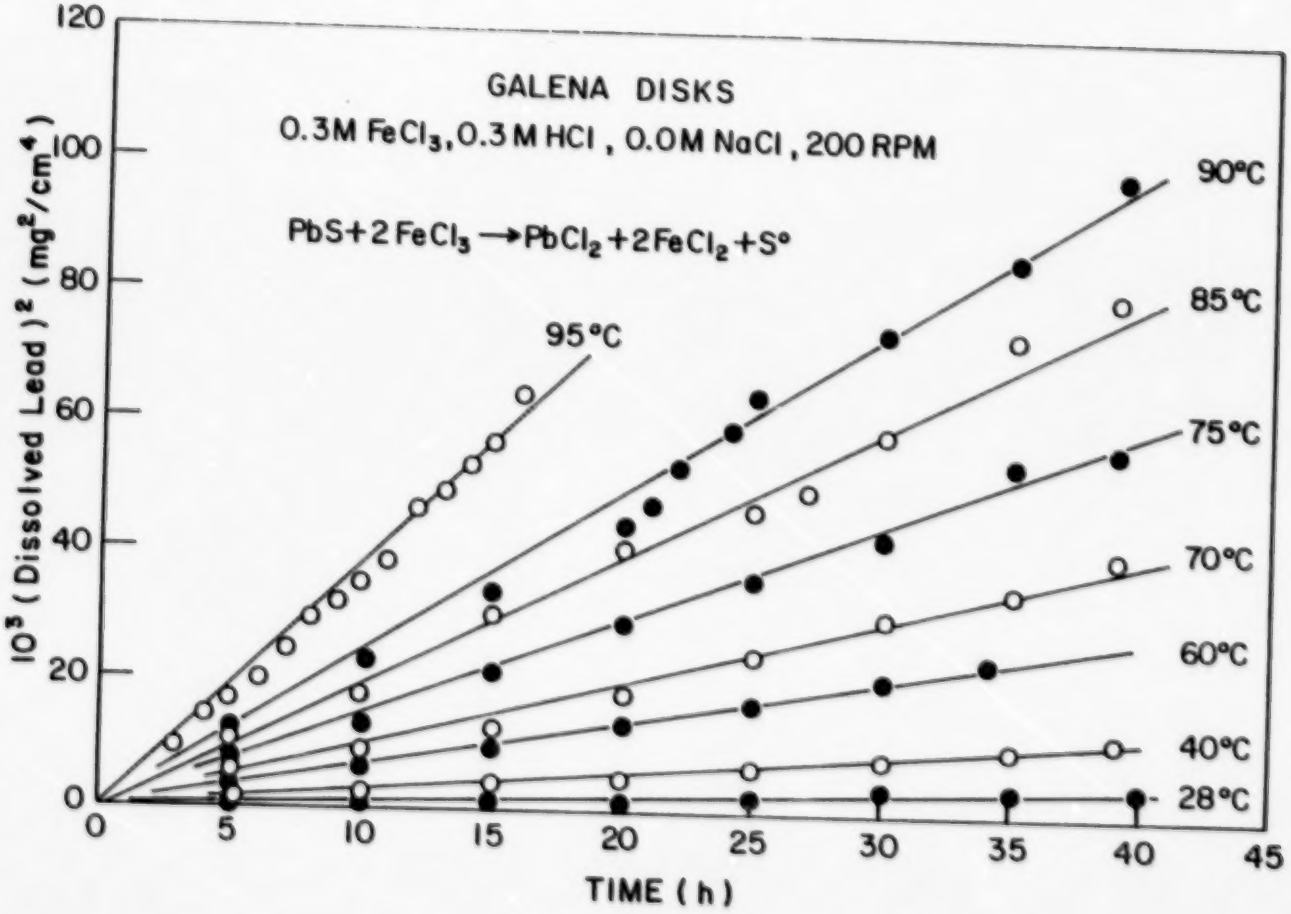

Fig. 7 - Leaching curves obtained for the dissolution of massive galena in 0.3 M $FeCl_3$ media at various temperatures. Data are plotted on a weight-squared versus time basis. Ref. 53.

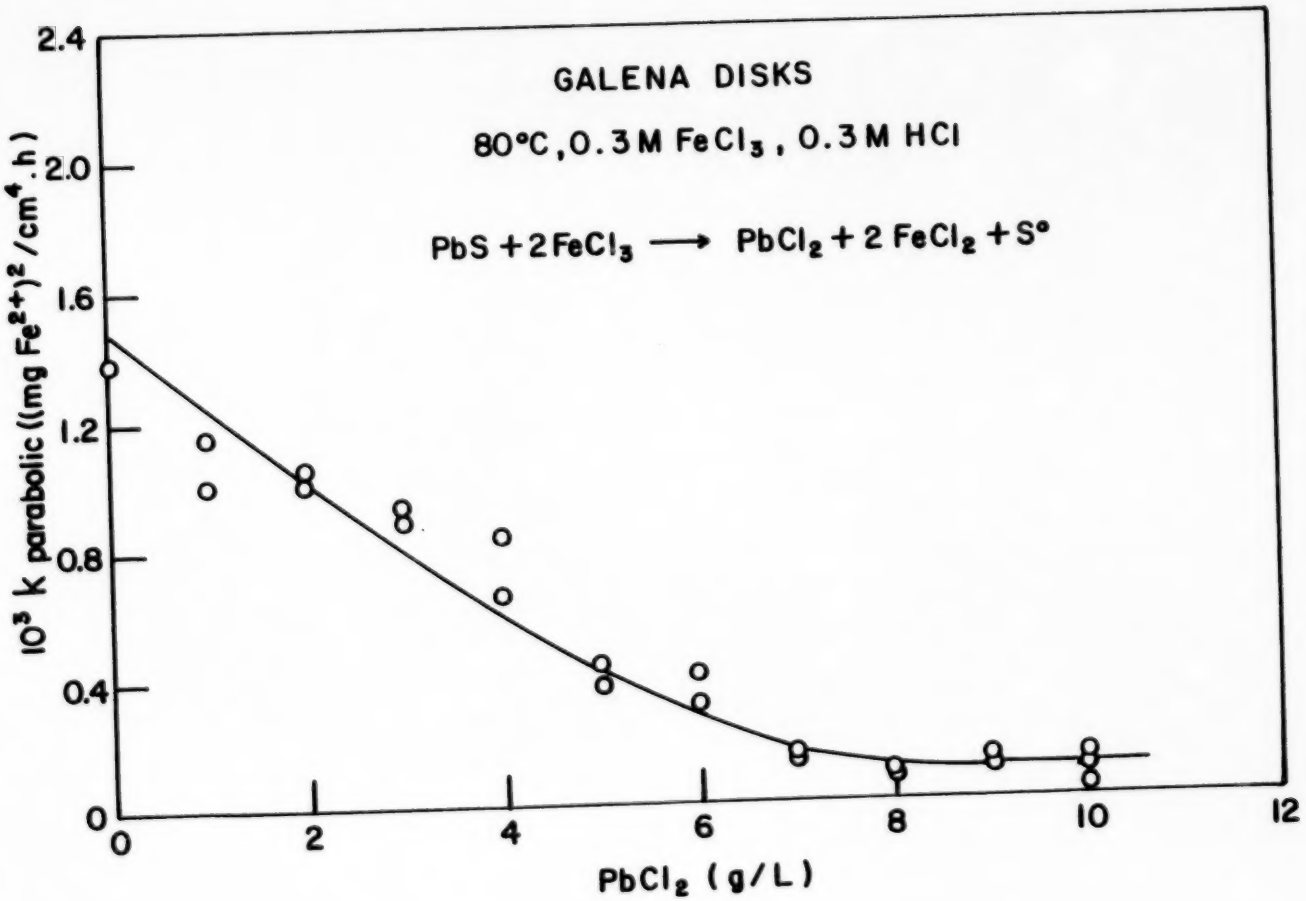

Fig. 8 - Effect of the lead concentration of the leaching medium on the parabolic rate constant for lead dissolution at 80°C. Ref. 53.

POOR

QUALITY

ORIGINAL